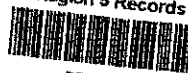


**MRC  
ENTERPRISES,  
INC.**

931043

EPA Region 5 Records Ctr.



351273

Office: 2901 Central Street, Evanston, Illinois 60201 U.S.A. 312/475-3400  
Sales: 1716 West Webster Avenue, Chicago, Illinois 60614 312/276-6345  
Cable Address: MATRECOM

February 16, 1984

FEDERAL EXPRESS MAIL

Mr. Del Haschemeyer  
Deputy Director  
Illinois Environmental Protection Agency  
2200 Churchill Road  
Springfield, Illinois 62706

Re: Cyanide Contaminated Film Chips

Dear Mr. Haschemeyer:

We appreciate your interest in our solution to eliminate the environmental hazards posed by the cyanide contaminated film chips located in and around the Chicago area. Enclosed is a description of our proposed solution.

Your field representative took samples at our demonstration on February 15, 1984, which when tested, should substantiate the validity of the process.

If it would serve your needs, representatives from Michigan Technological University would be willing to not only supply additional information but also expert court testimony should it be helpful.

Please call me at your earliest convenience so that we can answer any questions you may wish to have clarified.

Sincerely,

Aras G. Staniulis

GS/jw  
Enclosure

**RECEIVED**

WASTE MANAGEMENT DIVISION  
OFFICE OF THE DIRECTOR

CHEMICAL DESTRUCTION OF CYANIDE

AND

RESOURCE RECOVERY

A Patented Solution to the  
Cyanide Contaminated Film Chip Problem

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## I. INTRODUCTION

MRC Enterprises, Inc. of Chicago (MRC), and Michigan Technological University of Houghton, Michigan (MTU) are interested in providing a solution to the cyanide contaminated film chip problem that is plaguing the State of Illinois. This document includes background information about MRC and MTU. The cyanide problem is discussed along with the proposed elements of the solution. At the end of the discussion, a number of concluding and other pertinent comments are presented. We believe our solution provides the optimal environmental protection of all options considered, and also augurs some longer term economic benefit to the economy.

## II. MRC AND MTU EXPERIENCE

MRC and MTU are uniquely qualified to solve the cyanide contaminated film chip problem. MRC was organized four years ago for the purpose of reclaiming difficult-to-recover plastic materials, materials that require the creative application of known technology for their recovery. Over these four years MRC has grown into a million dollar company. It occupies a 40,000 square foot facility that has ample room to process the contaminated chips. (See Appendix A) Its key personnel are experienced plastics recyclers, environmental and professional engineers, and experienced businessmen. (See Appendix B) Briefly, MRC has the managerial, technical, physical, and financial capabilities to solve the cyanide contaminated chip problem in an economically and environmentally sound manner.

MTU owns patent rights to a process for the recovery of silver and terephthalic acid resources from exposed photographic film. This process is basic to this proposal. MTU's Bureau of Industrial Development is staffed with University engineers and scientists experienced both in basic research and in making practical industrial applications of that research. Its personnel are experienced in working with private industry in the solution of problems such as the elimination of the cyanide contaminated film chips. (See Appendix C and D).

## III. THE PROJECT

### A. Elements of the Problem

Of immediate concern is approximately 12 million pounds of cyanide contaminated film chips, although most assuredly there are other unknown sites harboring ever-growing stockpiles of contaminated chips. The subject material is either loaded in trailers or remains in unconfined piles on

warehouse floors. These piles are composed of incompatible plastics mixed together along with dirt, wood, stones, paper, and other unknowns. From the standpoint of plastics reclamation the greatest problem is presented by the presence of acetate film in varying concentrations intermixed with the desirable polyethylene terephthalate film.

The location of the material is in areas not suitable for processing. No matter how the material is processed and disposed, first it must be moved to another site. Obviously, the processing site must be environmentally, economically, and politically acceptable.

There are four possible processing and/or disposal alternatives that can be considered for the problem at hand. As for the first, landfilling, there is a movement away from chemical waste landfilling due to the unknown long-term risks and liabilities associated with it. Because no one can be certain of these risks, this alternative can be best compared with people expecting important guests at any moment and hastily sweeping the accumulated dust and dirt under their living room carpet, willing to wait until another day to sweep it out again for ultimate disposal. Also, there are the political aspects to consider when landfilling cyanide contaminated chips in other states. States are normally not receptive to burying problems of other states. Additionally, there is no recovery of the valuable resources, if the material is buried. It remains a potential liability without any benefits.

Chemical treatment is an alternative that affords only a partial solution. Its objective is to reduce the toxicity of the cyanide contaminated chips to the allowable limits for landfilling. Some believe the present cyanide concentrations allowed for landfilling are too high and, therefore, not environmentally safe. However, cyanide concentrations cannot economically be reduced any lower using current industrial methods. For this reason landfilling the treated film chips does not offer any significant advantages.

Incineration is a viable alternative except for a number of significant factors. Even so there remain several unanswered environmental questions involving incineration, including adequate assurance to the concerned public that no airborne contamination occurs. Also incineration involves significant toll charges. And again there is no recovery of valuable resources.

The proposed MRC/MTU method is a patented chemical destruction and resource recovery process that has been

developed to recover silver and terephthalic acid from spent photographic film without the use of cyanide. The process is similar to the patented Wet Oxidation Process, which is a proven method of cyanide destruction. In this application not only is cyanide destroyed, but one of the constituents of the film, terephthalic acid, is recovered. The only discharge from the process is a sewerable effluent with cyanide reduced to concentrations below 0.5 ppm.

The costs of treatment and disposal will not be inexpensive. It will require the investment of private and/or government funds. Whatever the investment and whomever the investing or funding source, the risks must be reduced as much as possible in order to ensure the successful resolution, i.e., elimination, of the environmental hazards in the Chicago area posed by the known storage sites of the contaminated film chips.

#### B. Elements of the Solution

We perceive the evaluation of four elements as being crucial to determining how to solve the cyanide contaminated chip problem. First, the destruction and/or disposal alternative should render the material chemically inert in a proven environmentally safe manner that is acceptable to the public. Legally safe might not be good enough. The chemical destruction of the cyanide combined with the recovery of terephthalic acid appears to be the most viable alternative.

Second, the contaminated material must be contained and secured in a safe manner. It must prevent public access to the stored material and the leaching of material into the ground water. Since the material is now located in areas neither compatible with processing nor disposal, it must then be safely moved. To accomplish this we propose bagging the chips in plastic preparatory to movement to the reclamation site. This will provide immediate containment of the material until ready for processing. Loaded in trailers the bags can then be safely moved to the production site at 1716 W. Webster Street in Chicago, where there exists the necessary building facilities with the required zoning. The bags will minimize human contact with the material, since the bags themselves will be processed along with the material.

Moreover, the presence of acetate film in varying concentrations in the cyanide contaminated material presents the main technical problem in our reclamation process. The process must be adjusted for the particular concentration of

acetate. Therefore, the material first must be statistically sampled to determine the acetate concentration. Also, the higher the concentration of acetate, the lower the production of terephthalic acid. With this variance the cost of reclamation will then increase proportionately.

The factors involving acetate also support the desirability of bagging the material. Bagging provides the means for properly mixing the chips during processing, to assure the uniformity of the acetate throughout the material and to yield the best quality terephthalic acid.

Third, there must be a timely solution. Subject to the capacity of the reclamation processing system, it must be understood that our processing will take about two years to complete. Construction of a 1,000,000 pound per month plant will allow reclamation to begin relatively quickly -- in about ten months.

Bagging will alleviate any concern over the time involved to complete our processing. We realize our process may require greater initial time than, say, landfilling. However, once completed, there is no lingering decades of concern over environmental effects, as there would be with landfilling, e.g. concern over leaching to the groundwater.

The fourth element of the solution involves the costs and risks associated with the processing of the cyanide contaminated material. We know the costs of our process, but we cannot quote an actual figure until the project is precisely defined. The costs will vary according to such factors as the scope of the project, the schedule of payments, the actual weight of contaminated chips needing processing, the concentration of acetate in the contaminated material, and the system redundancy required by the State of Illinois EPA for safety and other regulated aspects. Project financing can be arranged after a contract is signed with the State of Illinois, specifying the amounts and sequence of payments.

#### IV. CONCLUDING COMMENTS

MRC and MTU are interested in providing the solution to the cyanide contaminated film chip problem. We are already in the plastics reclamation business and we have already invested considerable funds to solve this problem. At the completion of the project, we will have taken in some 12 million pounds of waste deemed hazardous, chemically destroyed the cyanide and recovered terephthalic acid from the film chips.

This unique enterprise, involving private industry and a university, gives both a practical and scientific dimension to this solution. MRC handles millions of pounds of plastic scrap every year and MTU's patented Wet Oxidation process is currently in operation processing hazardous wastes in a large industrial installation.

The long run benefit of the patented process is that it replaces the need to use cyanide in the reclaiming of silver from photographic films. Using this Wet Oxidation process will eliminate the cyanide problem from recurring in the future. Thus, in accepting our solution, not only will an environmental problem be permanently solved, but a new Illinois based industry will be created.



APPENDIX A  
MRC FACILITY LAYOUT

MPC ENTERPRISES, Inc.

WEST GARDEN QUINN'S BUSH

R. Repair

NEW 10' x 10' HALL  
OFF DOOR

NEW 3' x 10' ENTRANCE  
DOOR

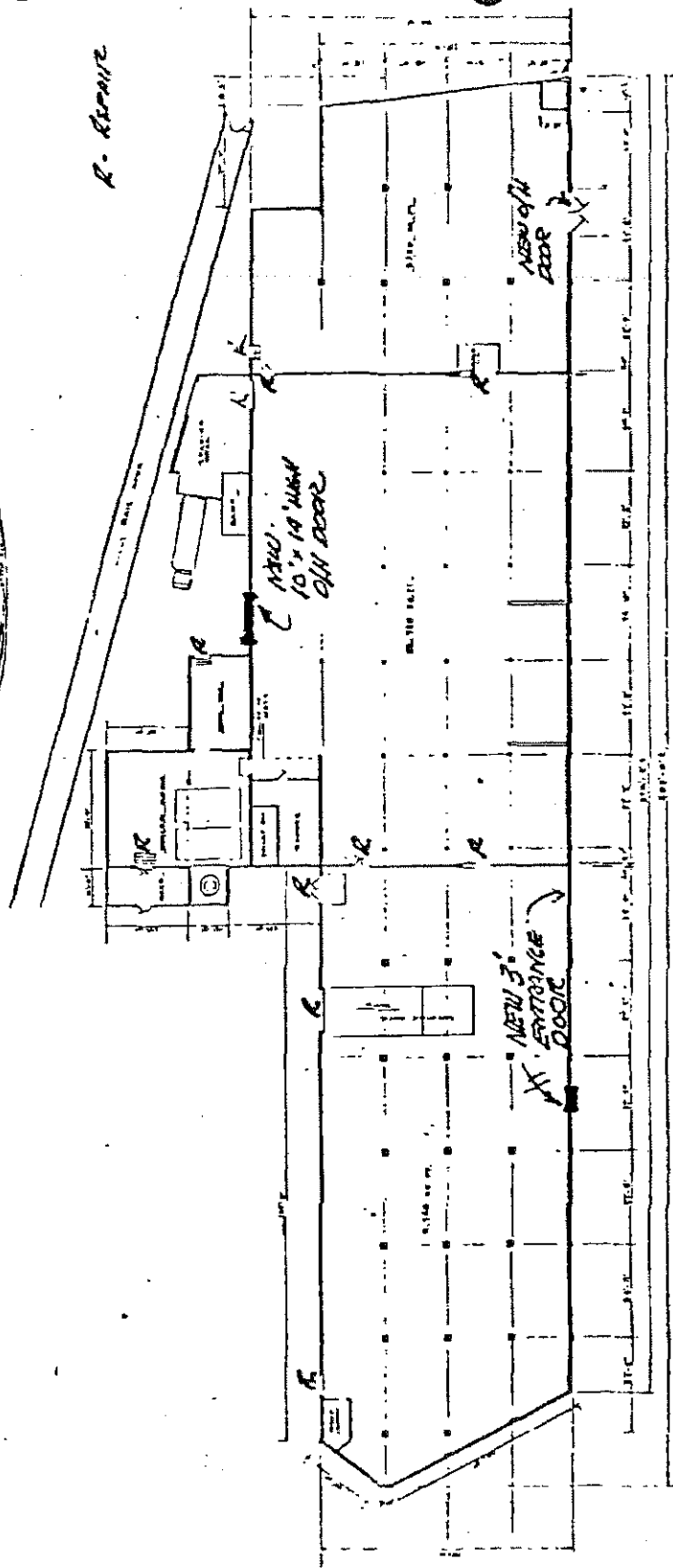
NEW 10' x 10' DOOR

EXECUTIVE LEASING DEPT.  
H. F. CHADDICK REALTY CO.  
100 W. MADISON ST.  
CHICAGO, ILLINOIS

INDUSTRIAL BUILDING 1716 WEBSTER (AT ELSTON)



TOTAL AREA 3400 SQ. FT.  
CEILING 10' 6" HIGHS 15' 6"  
THRU 17' HIGHS 20' 6"

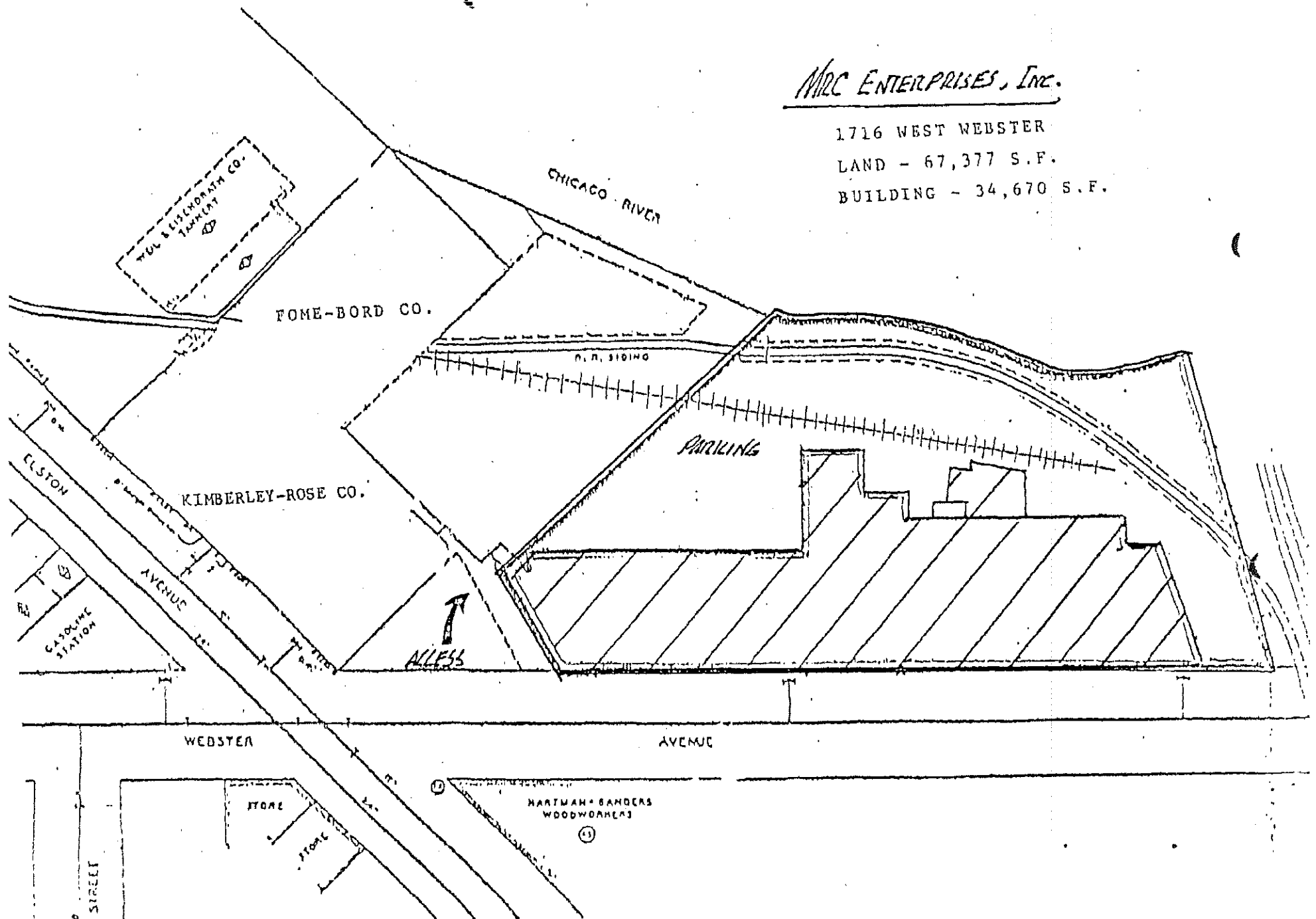


MRC ENTERPRISES, Inc.

1716 WEST WEBSTER

LAND - 67,377 S.F.

BUILDING - 34,670 S.F.



APPENDIX B  
MRC KEY PERSONNEL

MANAGEMENT OF MRC ENTERPRISES, INC.

The senior management of MRC Enterprises, Inc., consists of:

<u>Name</u>	
Aras G. Staniulis	Vice President
Daniel L. Eberhardt	President
John A. Wertymmer	Secretary/Treasurer

The following is a summary of the background of each of the persons named above:

1. Aras G. Staniulis

George Staniulis has worked in the plastics reclamation business for fourteen years. He began his career with Thermold Engineering, Inc., a subsidiary of Thorne United. This company was an integrated manufacturer of plastic tooling and molds, plastic vacuum forming and fabrication, and a manufacturer of vacuum forming equipment. There he acquired valuable on-line experience as a purchasing agent, production scheduler, and cost analyst.

Later Mr. Staniulis joined Eagle International Corporation, a thermo-plastic scrap reclaimer. As an Eagle Vice President for six years, Mr. Staniulis was totally responsible for opening their Los Angeles facility. There he operated a successful profit center and his responsibilities included developing new business, production, and marketing of plastic scrap throughout the United States and to other countries such as Spain and Taiwan.

During the past four years Mr. Staniulis has directed MRC Enterprises, Inc., in the areas of research and new product development.

In 1968 Mr. Staniulis graduated from Wayne State University, Detroit, Michigan, with a BS degree in marketing.

2. Daniel L. Eberhardt

Dan Eberhardt is an experienced manager, becoming the City Manager of the Borough of Greentree, Pennsylvania, at the age of

24, immediately after graduating from the University of Pittsburgh with a MBA degree. Mr. Eberhardt also holds a BS degree from Northwestern University in Environmental Engineering.

After a successful tenure in the public spotlight, Mr. Eberhardt returned to Chicago, where he worked for Thomas L. Jacobs & Associates, as a management consultant. Here he gained valuable experience analyzing the operations of several public "businesses", including the huge, multi-million dollar City of Chicago motor vehicle repair organization.

Four years ago Mr. Eberhardt founded Campus Painters, Ltd. The company now employs approximately 50 painters and carpenters and grosses close to \$1 million last year, making it by far the largest house-painting company on Chicago's affluent North Shore.

For the past two years Mr. Eberhardt has performed as President and General Manager of MRC Enterprises, Inc.

### 3. John A. Wertymer

John Wertymer has had major responsibilities in the start-up of numerous businesses in the years since he graduated with an MBA from the University of Chicago in 1969.

In his first job, Mr. Wertymer served as Assistant to the Chief Operating Officer of New Community Enterprises, the development of the Village of Park Forest South, Illinois. The company grew in four years from four to two hundred employees. During that time Mr. Wertymer's duties included line responsibilities such as Director of Engineering, Superintendent of Land Development, and Vice-President of the Park Forest South Utilities company. As Director of Engineering (Mr. Wertymer is a licensed Professional Engineer in the State of Illinois and a graduate of Civil Engineering from the University of Wisconsin), and as Superintendent of Land Development, he administered the planning, designing, and construction of millions of dollars of land improvements. As Vice President of the Utilities Company (he was a licensed Wastewater Treatment Plant Operator in the State of Illinois), he was responsible for a multi-million dollar expansion program of the wastewater treatment plant and the water supply system, including pumping stations and water storage reservoirs. In conjunction with the environmental studies faculty at Governors State University he applied for and received Federal approval for a 4.0 million dollar wastewater recycling system. He handled presentations to the Illinois EPA, U.S. EPA, NIPC, and the ICC.

APPENDIX C

MTU PATENTS AND  
KEY RESEARCH PAPER

# United States Patent [19]

Fassell et al.

[11] 3,953,502

[45] Apr. 27, 1976

[54] RECOVERY OF SILVER AND  
TEREPHTHALIC ACID COMPONENTS  
FROM LIGHT SENSITIVE FILM  
MATERIAL

3,658,894 4/1972 Juveland et al. ....260/525  
3,317,519 5/1967 Lazarus et al. ....260/239.3  
2,131,072 9/1938 Reid .....75/118

[75] Inventors: W. Martin Fassell, Newport Beach,  
and Donald W. Bridges, Irvine,  
both of Calif.

Primary Examiner—Anton H. Sutto  
Attorney, Agent, or Firm—McDougall, Hersh &  
Scott

[73] Assignee: Barber-Colman Company,  
Rockford, Ill.

[22] Filed: May 1, 1974

[21] Appl No. 466,015

[52] U.S. Cl. .... 260/525; 260/515 P; 423/23;  
423/35

[51] Int. Cl.<sup>2</sup> ..... C07C 51/42; C01G 5/00

[58] Field of Search ..... 260/525, 515 P, 475 D;  
423/23, 35; 75/118 DIG. P

## [56] References Cited UNITED STATES PATENTS

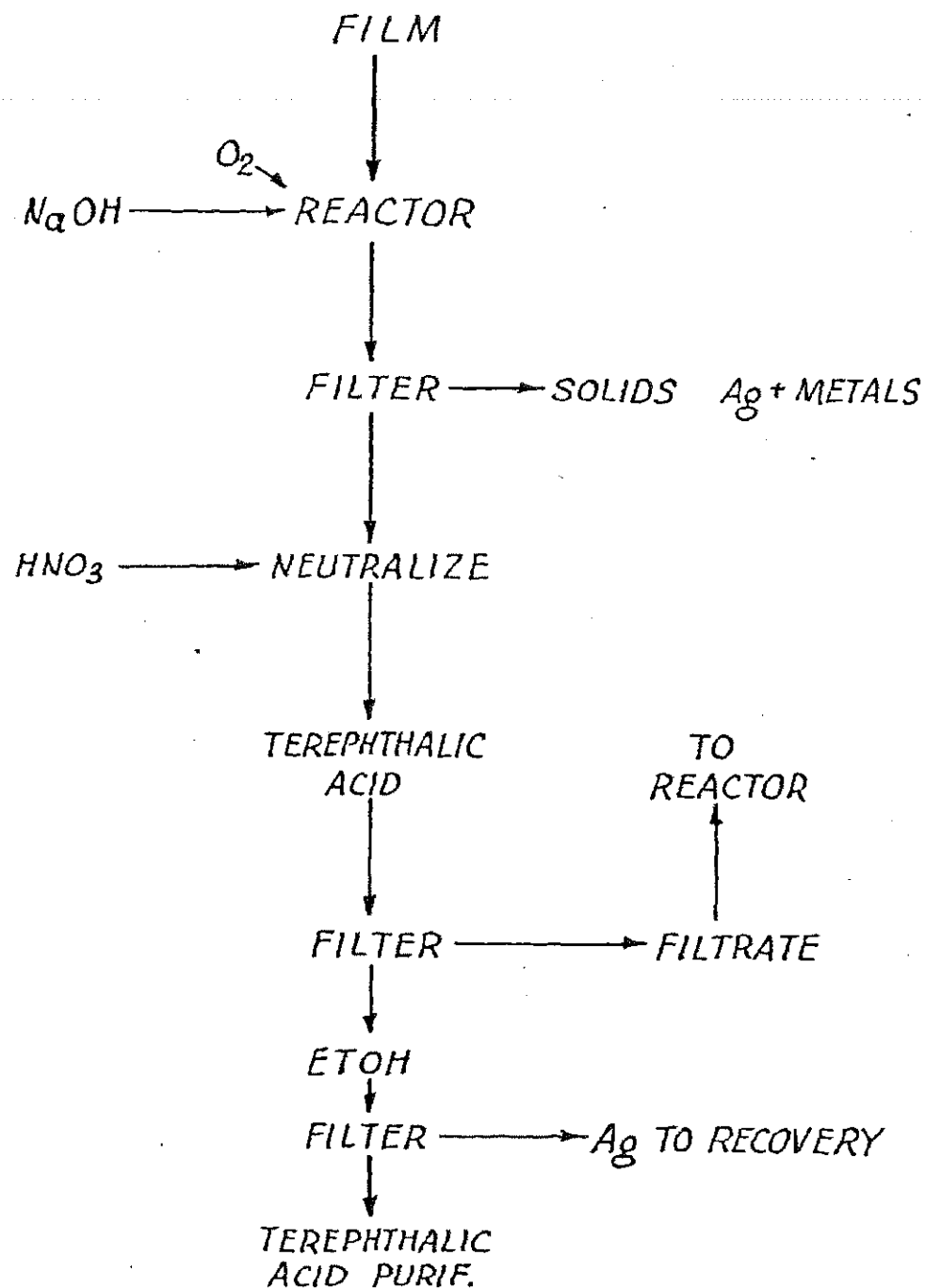
3,544,622 12/1970 England .....260/515 P  
3,020,312 2/1962 Moscrip .....260/525

## [57] ABSTRACT

The process for the recovery of silver and terephthalic acid component from scrap film of a light sensitive silver compound on a Mylar substrate in which the film is subjected to at least a partial wet oxidation in an aqueous alkaline medium at elevated temperature and pressure whereby the Mylar substrate is depolymerized into components which remain soluble in the liquid reactant while the silver component remains insoluble therein to enable separation of the silver component and the subsequent recovery of terephthalic acid component by acidification of the liquid phase.

16 Claims, 1 Drawing Figure





# RECOVERY OF SILVER AND TEREPHTHALIC ACID COMPONENTS FROM LIGHT SENSITIVE FILM MATERIAL

This invention relates to the disposal of photographic or X-ray film and particularly to the disposal of exposed and unexposed photographic or X-ray film of the type formed of a silver halide emulsion coating on a base formed of Mylar (methyl terephthalic-ethylene glycol polyester), and still more particularly to the disposal of such material in a manner which enables substantially complete recovery of silver from the emulsion coating and the terephthalic acid component from the film base, and in which such disposal and recovery can be carried out in a pollution-free manner.

In our copending application filed concurrently herewith, and titled "The Process for the Destruction of Developed and Undeveloped Photosensitive Film and the Recovery of Products Therefrom", Serial No. 465,801, filed May 1, 1974, description is made of a process for the destruction of developed or undeveloped photosensitive film of silver halide emulsion on various organic substrates, by wet oxidation at elevated temperature and pressure, in aqueous medium containing a silver complexing component, such as an amine or ammonia, whereby the silver released from the coating on the substrate is converted to a soluble silver complex while the organic substrate material is consumed during the wet oxidation process or partially oxidized to usable organic components which can be recovered from the effluent of the wet oxidation reaction. The silver is separated from the solution by conversion of the silver from the soluble complex to an insoluble salt, such as by the addition of sulphuric acid to convert the silver complex to a separable insoluble silver sulphate; or by electrowinning the silver from the solution in which an acid, such as nitric acid, is added to enable plating out of the silver from the solution; or by reduction with hydrogen or other reducing agent to convert the silver from the soluble complex to metal solids which can be recovered by conventional solid-liquid separation techniques.

In the process described in the copending application, the formation of undesirable silver azides is possible and processing to maximize the recovery of silver requires treatment of the liquid phase, after silver separation, since some of the silver still remains in solution.

It is an object of this invention to provide a method for the processing of scrap light sensitive film, including exposed or unexposed light sensitive material, in which the recovery of silver is maximized, in which such recovery can be made in a simple and efficient manner with the expenditure of a minimum amount of time, materials, equipment and labor, in which when the film base is formed of Mylar or other terephthalate polyester, the terephthalic acid component can be recovered in good and economical yields, and wherein such recovery processes can be carried out without polluting the environment and with the elimination of scrap film as a potential pollutant.

In accordance with the practice of this invention, the Mylar based film, with the exposed or unexposed

silver emulsion coating, is segmented as by cutting, chopping, beating, or other means of subdivision into relatively small particles which are then subjected to wet oxidation and preferably partial wet oxidation in an aqueous alkaline medium, with constant agitation, and at elevated temperature and pressure, for a time sufficient to effect cleavage of the polyester for separation of the terephthalic acid component. The breakdown of the polymer and the cleavage between the terephthalic acid component and the glycol of which the Mylar is formed is believed to result from a combination of hydrolysis and oxidation under the operating conditions existing within the reactor.

While wet oxidation beyond the minimum to achieve depolymerization and cleavage can be employed without jeopardizing the recovery of silver, it is desirable to minimize the amount of excessive oxidation if recovery of the terephthalic acid component is an objective, since additional wet oxidation will result in additional combustion of the dissolved organic phase, with corresponding reduction in chemical oxygen demand (COD) of the solution and corresponding loss of terephthalic acid component.

Under the operating conditions described for complete and preferably partial oxidation of the organic film substrate, the undeveloped silver halide or the reduced silver in the exposed portion of the emulsion coating remains insoluble while the organic film base is reduced to a soluble state thereby to enable simple and efficient separation of the silver phase by conventional solid-liquid separation means, such as by filtration, centrifugal separation, decantation, and the like. The terephthalic acid component, dissolved in the liquid phase, after separation of the silver component, can be recovered by acidification of the alkaline solution whereupon the terephthalic acid component precipitates since it has very low solubility in aqueous acid medium (less than 0.02 grams per liter at 25°C).

Light sensitive silver halide coatings on film Mylar substrates represent a large segment of the market. X-ray film, often referred to in the trade as "medical green" is a major factor in the total film market and is almost entirely formed with a Mylar substrate. The photographic film market and the movie film market is increasingly making use of Mylar as the film substrate. Since terephthalic acid represents a valuable ingredient, currently in short supply, considerable interest is expressed in the recovery of terephthalic acid either as a principal product, or as a by-product, from the destruction of exposed or unexposed film and the recovery of silver therefrom.

The process of this invention will hereinafter be described by reference to the following examples 1 to 15, and the accompanying flow diagram. The examples are given by way of illustration and not by way of limitation of the invention.

The following is an identification of the various film materials that were processed in the examples:

Film Code	General Description	Silver content, % w	Other
MG	Medical Green X-ray Film, unexposed	3.6	6.5 moisture 86.2 volatiles 7.3 residue
BLC	Industrial lithographic film, non-Mylar base, exposed	1.1 (clear) 2.7 (dark)	- -

Film Code	General Description	Silver content, %w	Other
HEK	Paper-based film, exposed	-	-
VI	Black industrial X-ray film, exposed	-	-
FM	Teat medical, non Mylar base, exposed	-	-
CP	Mixture of film from Naval Ordnance demonstration tests at Camp Pendleton exposed	-	-

## EXAMPLES 1-15

The runs of Examples 1-15 were each carried out in an autoclave reactor having a capacity of one gallon and with the cylinder, baffle and stirrer formed of titanium.

In each example, the reactor was charged with 1470 ml of distilled water and the calculated amount of film and base material, and the stirrer was operated at 1000 r.p.m.

The autoclave was then closed and the specified amount of oxygen was added as pure oxygen. The temperature within the reactor was raised to a specified reaction temperature and the reaction was continued for a time, all as hereinafter set forth in the accompanying tabulation.

At the conclusion of the run, the reaction mixture was cooled rapidly by external water quench and the reactor was then opened. The cylinder was examined and the reaction product analyzed for the materials contained therein.

The effluent from the reactor was filtered to remove the insolubles which included the recoverable silver and silver halide components.

The filtrate was then acidified with nitric acid to precipitate the terephthalic acid component which was filtered off and then purified to remove entrained silver by resuspension in ethyl alcohol and filtering. Entrained silver remains with the filtrate while the purified terephthalic acid component separates as a solid.

Before each run, the reactor was thoroughly cleaned with a nitric acid rinse, followed by cleaning with a scouring powder. In Example 5, the reactor was further purged by pressurizing and depressurizing with nitrogen gas to eliminate any oxygen that might have been present.

In the examples, variations were made in the mean reaction temperature, reaction time, base material and film stock, as set forth in the following tabulation, to determine the effect of these variables on the recovery of silver, terephthalic acid component, and combustion of organic material. Examples 6 and 10 were atypical on account of low pH and other variables but were included for purposes of comparison.

All of the analyses recorded in the following tabulation were carried out in accordance with the procedures detailed in the EPA manual titled "Methods for Chemical Analysis of Water and Wastes-1971".

The reaction mixture was measured for pH, chemical oxygen demand (COD), and for silver by atomic absorption. Cylinder liquid was tested for filterable solids on a No. 1 medium grade Whatman filter paper and terephthalic acid component (TPA). The latter involved acidification of the filtered liquid with nitric acid and subsequent gravimetric determination of the the precipitate of terephthalic acid component removed on the filter. The percentage recovered TPA was based on the assumption that all of the non-moisture, volatile residues in the film were pure Mylar polyester. The ultimate or stoichiometric TPA content was calculated in accordance with the following equation:

$$30.0 \text{ grams film} \times 0.8625 \frac{\text{grams volatiles}}{\text{gram film}} \times \frac{1 \text{ gram polymer}}{1 \text{ gram volatiles}} \times \frac{166 \text{ grams TPA}}{192 \text{ grams polymer}} = 22.37 \text{ grams TPA}$$

The recovered terephthalic acid component was characterized by IR analysis. Two important evaluations were the COD and silver content in the final liquid effluent. As a basis for comparison, the theoretical total COD of effluent, using medical green film, is about 34,500 mg/l O. The theoretical silver level in the final effluent would run between 900 and 1200 ppm if totally dissolved. For the purpose of this evaluation, no quantitative material balance was attempted on silver beyond showing its absence in the filtered liquid effluent. As the results discussed hereinafter indicate, the silver contents of the filtered effluents from all the tests were very low compared to the theoretical potential level of 1000 ppm. This is believed to establish that the silver was separated from the water soluble TPA salt.

TABLE I

Summary of Process and Analytical Data from Film Hydrolysis Study

Test No.	Principal Variables					Analytical Results						
	Mean Temp. (°F)	O <sub>2</sub> Level (mg)	Run Time (min)	Base	Amt. Base (lb) Stoch.	Film	TPA (2) Recov. %	Silver (3) in Filtr. (ppm)	S.S. (4) in Liq. (ppm)	COD (5) mg/l O	% of COD (6) Due to TPA	Silver (7) in Digest (ppm)
1	46.4	30,160	150	NaOH	835	Med. Gr.	83.4	0.4	1006	21,733	84.1	-
2	40.0	31,020	150	NaOH	176	Med. Gr.	95.0	0.4	1352	28,450	73.4	1200
3	35.3	30,575	129	NaOH	176	Med. Gr.	99.1	2.8	876	31,962	67.5	350
4	32.9	30,640	124	NaOH	176	Med. Gr.	93.6	3.1	754	29,802	68.8	-
5	39.4	32,131	138	NaOH	176	Med. Gr.	67.5	0.4	1201	29,371	53.4	-
6	37.2	32,160	12.5	NaOH	176	Med. Gr.	-	1.3	4671	22,360	-	-
7	30.5	32,360	121	NaOH	176	Med. Gr.	12.2 (8)	4.7	2276	15,881	17.0	-
8	39.7	32,360	129	NaOH	38	Med. Gr.	0.9 (9)	0.1	4517	18,275	5.1	-
9	39.6	30,575	138	NaOH	76	Med. Gr.	52.7	0.1	5067	25,939	42.9	-
10	38.6	30,575	39	NaOH	176	Med. Gr.	89.2	2.6	172	29,288	66.1	350

Table I-continued

Summary of Process and Analytical Data from Film Hydrolysis Study

Test No.	Principal Variables						Analytical Results					
	Mean Temp. °F	O <sub>2</sub> Level mg	Run Time min	Base	Amt. Base (1) Stoich	Film	TPA (2) Recovery, %	Silver (3) in Filtrate, ppm	S.S. (4) in Liq. ppm	COD (5) mg/l 0	% of COD (6) Due to TPA	Silver (7) in Digest FE, ppm
11	399	29,680	129	KOH	176	Med Gr.	81.4	5.0	1084	28,106	62.8	—
12	390	31,020	145	Na <sub>2</sub> CO <sub>3</sub>	176	Med Gr.	94.2	0.3	573	28,697	71.9	—
13	399	31,915	125	NaOH	176	BLC	—	1.2	1452	20,985	—	390
14	396	32,360	130	NaOH	176	Mixed (10)	72 (6) (11) (12)	1.7	1020	21,480	36.1	—
15	439	30,575	134	NaOH	176	ITEK	—	0.1	256	10,162	—	—

(1) Percentage of stoichiometric base required to form the sodium salt of terephthalic acid (TPA).

(2) Based on theoretical TPA content assuming non-moisture, volatile are 100% Mylar.

(3) Silver dissolved in liquid at end of reaction.

(4) Suspended solids in cylinder liquid which are removed by simple filtration-normalized to account for per volume.

(5) COD-normalized to account for per volume and COD content.

(6) Percentage of COD due to recovered TPA.

(7) Silver in final effluent after solids were digested with acid.

(8) Also recovered unhydrolyzed film (52% of charge).

(9) Impure TPA, unhydrolyzed film remained.

(10) Mixture of 75 grams of each of the following: Black industrial, Camp Pendleton, tear medical and ITEK.

(11) Based on assumption that the Mylar based films—B1 and CP—have similar Mylar content to that of med. green.

(12) Cellulose fibers remained.

The role of oxygen in the wet oxidation process is indicated by comparison of Examples 2, 4 and 5, wherein the oxygen level was varied from 31,020 mg in Example 2, to 660 in Example 4, and the complete absence of oxygen in Example 5. It will be seen that silver recovery, as indicated by the absence of silver in the filtrate, was equally low (0.4 ppm in the filtrate) with and without oxygen, indicating that the separation of silver from the film base was not oxygen dependent. On the other hand, the amount of terephthalic acid component recovered was considerably less in the absence of oxygen, indicating that at least partial oxidation in the alkaline wet oxidation process is beneficial to the cleavage of the polyester into its components.

The amount of oxygen introduced is therefore not significant by comparison of Examples 2 and 4 from the standpoint of the TPA recovery, but it is desirable to have oxygen present to provide for at least partial oxidation of the organics present in the system.

The oxygen can be added as pure oxygen, in the desired amount in a batch operation, but from a practical standpoint and for commercial practice wherein the recovery process can be carried out on a continuous or semi-continuous basis, it is desirable continuously to introduce the oxygen into the reaction medium, in the form of an oxygen containing gas such as pure oxygen, and preferably in the form of air.

For this purpose, use can be made of a wet oxidation reactor, such as described in our pending applications Ser. No. 400,123 filed September 24, 1973, now U.S. Patent No. 3,870,631, and Ser. No. 403,652 filed October 4, 1973 now U.S. Patent No. 3,852,192.

By comparison of Examples 1, 2 and 3, it will be seen that the amount of combustion of organics in the reaction mixture is proportional to the reaction temperature, with but little actual reduction in COD occurring at a reaction temperature of 353°F (Example 3) or below, and with increasing reduction of COD at higher reaction temperatures such as the 400°F of Example 2 and 464°F of Example 1. Nevertheless, the amount of silver remaining in the reaction

mixture after filtration is seen to be somewhat independent of the amount of oxidation under the conditions described.

Relatively low susceptibility of TPA to wet oxidation, by comparison with other organics in the liquor, is indicated by the lesser reduction in COD due to TPA by comparison with the entire system. This indicates that the terephthalic acid factor remains substantially high under the reaction conditions described to make it interesting to provide for commercial recovery of the TPA as well as the silver from scrap film.

From a comparison of Examples 1, 2, 3 and 7, it will be seen that recovery of TPA is at a maximum at a reaction temperature of about 350°F with little, if any, decrease in recoverable TPA up to 400°F. Thus it is desirable to make use of a reaction temperature of at least 350°F with the upper temperature limits being dictated more by economics and safety factors, since the autogenous pressures maintained within the reactor are temperature dependent. In the preferred practice of the invention, use is made of a reaction temperature within the range of 325°-425°F and preferably within the range of 350°-375°F, at corresponding autogenous pressure for a closed system.

Example 10 indicates that reaction time of 30 minutes is sufficient at reaction temperatures of 400°F and at a pH of 12.8 to 13.2. Longer reaction times are desirable at lower reaction temperatures, such as 60 minutes at 350°F, but within the preferred temperature range of 350°-375°F, a minimum of 10 minutes and a maximum of 180 minutes is employed, with the preferred reaction time being within the range of 30 to 60 minutes.

The amount of base in the reaction mixture, subjected to wet oxidation, bears considerable influence on the amount of TPA that is made recoverable by the process of this invention. This can best be expressed by the theoretical amount of base required to react with the TPA to neutralize the acid and from the corresponding metal salt thereof. The values

given in the table are calculated on the stoichiometric amount as 100%. Thus the value of 38% in Example 8, and 76% in Example 9, indicates an amount corresponding to about 38 and 76, respectively, of the stoichiometric amount of base whereas the value of 176% indicates an excess of 76% over the stoichiometric amount. It will be apparent from a comparison of Examples 8 and 9 with Examples 1, 2 and 3, for instance, that with an amount of base less than stoichiometric, the recovery of TPA falls off considerably to practically zero recovery at 38% of the stoichiometric amount. The recovery of TPA drops only gradually above 200% of the stoichiometric but it is undesirable to make use of an amount of base in excess of 900% of the stoichiometric amount.

The amount of base can also be expressed from the standpoint of pH of the reaction mixture. For instance, at a pH of less than 9, the recovery of TPA is quite low. Best results are secured at a pH within the range of 10 to 14 and preferably within the range of 12 to 13.5.

As the base, it is preferred to make use of a strong base such as an alkali metal hydroxide or carbonate. As indicated by Examples 2, 11 and 12, it is preferred to make use of sodium hydroxide or sodium carbonate by comparison with potassium hydroxide, when measured from the standpoint of the silver which remains dissolved in the liquid filtrate after separation of the silver solids from the product of the wet oxidation reaction. 5 ppm silver remains in the filtrate formed with a base of potassium hydroxide, Example 11, whereas only 0.4 ppm and 0.3 ppm remains for sodium hydroxide, Example 2, or sodium carbonate, Example 12. Apparently the silver is more soluble in a potassium hydroxide solution than in a solution of sodium hydroxide or carbonate at equivalent pH.

Examples 13, 14 and 15 were runs made on film other than medical green. As indicated heretofore, Itek film is not formed with a Mylar substrate so that no TPA was recovered. Nevertheless, the recovery of silver was very high as indicated by less than 1 ppm of silver in the filtrate remaining after silver separation.

In Example 14, the film treated was made up of a mixture of Itek, Black Industrial X-ray film (BI), Tear Medical film (TM) and a mixture from Naval Ordnance (CP). All of the non paper based films were hydrolyzed and the contained silver was precipitated. However, fibrous residues from the paper based Itek film were left behind. In Example 15, the Itek film was reacted at higher temperature (450°F) which brought about wet oxidation of the paper and thus eliminated solid organic residues. As with medical green, only trace silver was present in the effluent filtrated from these examples.

It will be apparent from the foregoing that we have provided a process for separation and recovery of silver and terephthalic acid from Mylar based photographic film. The film can be readily solubilized in aqueous alkaline solutions at temperatures above 300°F even in the absence of oxygen. If no oxygen is present, apparently about 33% of the TPA from the Mylar is tied up as acid soluble species since only about 67% of the TPA is recovered upon acidification. In the presence of relatively small amounts of oxygen, essentially all of the TPA in the film is solubilized as free sodium terephthalate. The silver

which remains insoluble is easily removed from the solubilized TPA in the product of the wet oxidation reaction.

If both TPA and silver are desired as products, the use of relatively low temperature with a small amount of oxygen represents the preferred practice. Under these conditions, TPA recovery is maximized while capital costs for equipment is maintained at a minimum. For special film types and for minimum COD discharge from the system, the process can be carried out at higher oxygen and temperature levels.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A process for the treatment of a polyester formed of terephthalic acid for the recovery of terephthalic acid and silver when present therewith as a light sensitive compound comprising subjecting the polyester to at least partial wet oxidation at elevated pressure and a temperature of at least 325°F in an aqueous alkaline medium having a pH of at least 9 and into which an oxygen containing gas is introduced in an amount to provide at least partial oxidation of the organics present whereby any silver component present remains in the solid phase and the terephthalic acid component is contained in the liquid phase in a dissolved state, separating any solid phase from the liquid phase, acidifying the liquid phase to precipitate the terephthalic acid component, and then separating the terephthalic acid component from the remainder.

2. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a temperature within the range of 325°-425°F.

3. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a temperature within the range of 350°-375°F.

4. The process as claimed in claim 1 in which at least partial wet oxidation reaction is carried out for a time of at least 10 minutes.

5. The process as claimed in claim 1 in which at least partial wet oxidation reaction is carried out for a time within the range of 10 to 180 minutes.

6. The process as claimed in claim 1 in which at least partial wet oxidation reaction is carried out for a time within the range of 30 to 60 minutes.

7. The process as claimed in claim 1 in which the aqueous alkaline solution has a pH above 9.

8. The process as claimed in claim 1 in which the aqueous alkaline solution has a pH within the range of 12 to 13.5.

9. The process as claimed in claim 1 in which the aqueous alkaline solution is formed with a highly basic material present in an amount of at least 100% of the stoichiometric amount required to form the alkali metal salt of the terephthalic acid component.

10. The process as claimed in claim 1 in which the aqueous alkaline solution is formed with a highly basic material present in an amount within the range of 100% to 200% of the stoichiometric amount required to form the alkali metal salt of the terephthalic acid component.

11. The process as claimed in claim 9, in which the highly basic material is an alkali metal hydroxide or carbonate.

12. The process as claimed in claim 11 in which the

basic material is selected from the group consisting of sodium carbonate and sodium hydroxide.

13. The process as claimed in claim 1 in which the liquid phase after separation of any insoluble silver component is acidified with nitric acid to precipitate the terephthalic acid component.

14. The process as claimed in claim 1 which includes the step of recovering the silver when present from the solid phase separated from the wet oxidation reaction product.

15. The process as claimed in claim 1 which includes the step of purifying the separated terephthalic acid component by treating the separated terephthalic acid component with an alcohol to dissolve out any

silver retained with the terephthalic acid component.

16. A process for the treatment of scrap polyester formed of terephthalic acid for the recovery of terephthalic acid, comprising subjecting the polyester to at least partial wet oxidation in an aqueous alkaline medium at elevated pressure and at a temperature of at least 325°C and at a pH of at least 9 whereby the terephthalic acid component is contained in the dissolved state in the liquid phase, separating any solids from the liquid phase, acidifying the liquid phase to precipitate the terephthalic acid component, and then separating the terephthalic acid component from the remainder.

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## United States Patent [19]

Fassell et al.

[11] 3,956,088

[45] May 11, 1976

[54] PROCESS FOR THE DESTRUCTION OF DEVELOPED AND UNDEVELOPED PHOTSENSITIVE FILM AND THE RECOVERY OF PRODUCTS THEREFROM

[75] Inventors: Wayne Martin Fassell, Newport Beach; Donald W. Bridges, Irvine, both of Calif.

[73] Assignee: Barber-Colman Company, Rockford, Ill

[22] Filed: May 1, 1974

[21] Appl. No. 465,801

[52] U.S. Cl. .... 204/109; 75/118 R;

75/118 P; 75/101 R

[51] Int. Cl.<sup>1</sup> ..... C22D 1/12; C22B 11/04

[58] Field of Search ..... 75/118 P, 118; 204/109

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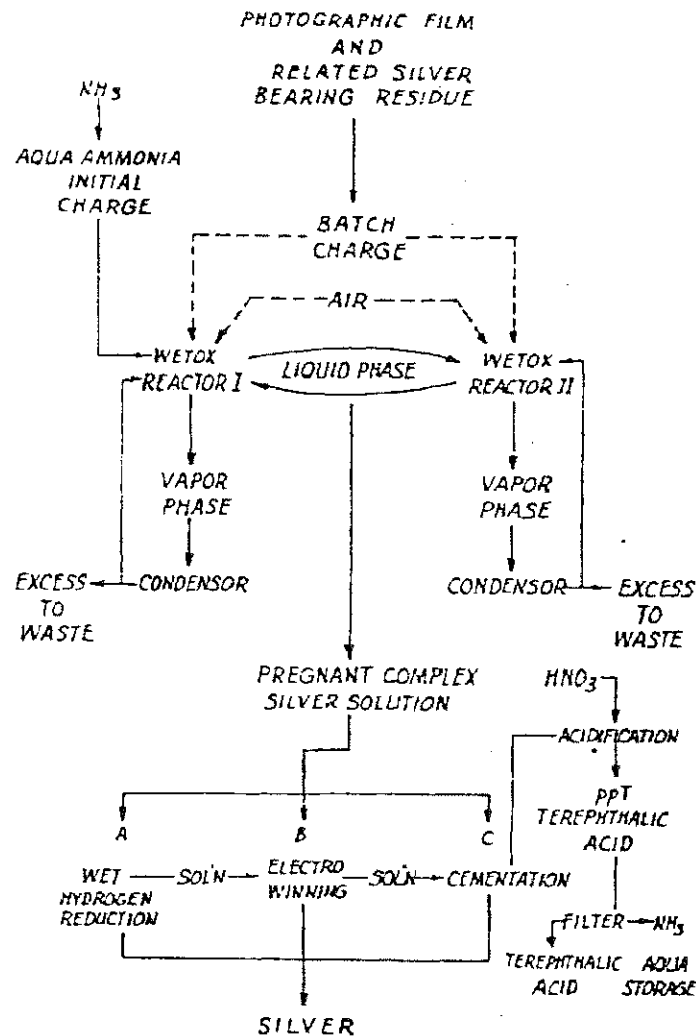
Primary Examiner—G. Ozaki  
Attorney, Agent, or Firm—McDougall, Hersh & Scott

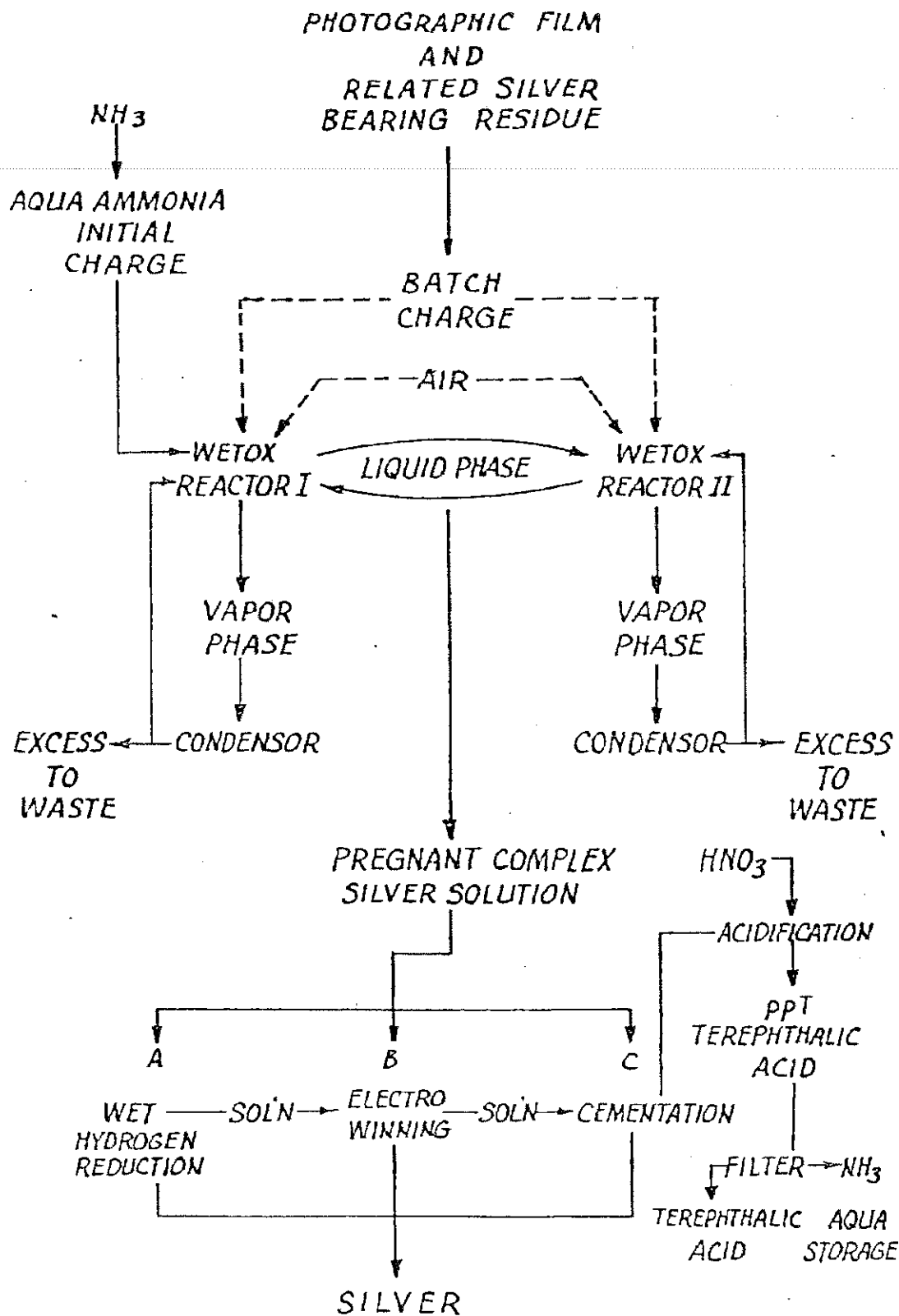
## [57] ABSTRACT

The destruction of developed or undeveloped photographic film in a manner which permits also the recovery of silver and organic components from the film material in which the film is subjected to wet oxidation at high temperature and high pressure in the presence of a wet oxidation catalyst and a silver complexing compound, and then subjecting the liquor from the wet oxidation step to processing to separate the solubilized silver which is freed from the film and to separate components derived from the film material in the liquor that remains.

20 Claims, 1 Drawing Figure

Research Division  
MICHIGAN TECHNOLOGICAL UNIVERSITY  
Houghton, Michigan 49931  
(906) 487-2225







# PROCESS FOR THE DESTRUCTION OF DEVELOPED AND UNDEVELOPED PHOTOSENSITIVE FILM AND THE RECOVERY OF PRODUCTS THEREFROM

This invention relates to the recovery of silver and organic by-products from developed or undeveloped light-sensitive emulsion on film, paper or the like base material.

An extensive use is made of photographic film for surveillance, non-destructive testing, medical radiography, data storage, and the like, in addition to the mass utilization of photographic film in cameras, the movie industry, and home movies, wherein the silver emulsion is usually provided on a transparent or translucent film substrate formed of Mylar, triacetate and the like. Similarly, in such copy processes as the diffusion transfer process, for single copy work and master preparation, or in the photocopy of the Polaroid type, considerable use is made of silver halide emulsions on substrates, usually in the form of high wet strength paper or plastic film of the type heretofore described.

A considerable amount of the material ends up as waste and represents a large reserve of silver which, because of its high intrinsic value and projected short supply, should be recovered.

Various techniques have been proposed for the recovery of silver from waste of the type described. In one process, the film is chopped and shredded to liberate the emulsion from the film base. The finely divided material is slurried with water to effect flotation of the film base while the heavier silver emulsion settles to the bottom of the flotation tank. The settled underflow is subjected to centrifugal separation to concentrate the silver salts, which can then be smelted to form ingots or bars of impure silver capable of being refined by the Thum process. Recovery by the described process is expensive and often incomplete.

In another process, the photographic film is incinerated and pyrolyzed as by the use of molten salts wherein reduced silver accumulates as droplets and settles to the bottom of the molten salt bath. In this process, a considerable amount of the silver is lost by volatilization and by incomplete reduction, while the organic film base is lost by combustion with the release of undesirable gases which pollute the atmosphere.

Many attempts have been made, in recent years, to salvage the film base for re-use. These approaches have not found commercial success since the cost of recovery is relatively high and the market for such salvaged base material is limited. However, where classified data are involved, it is necessary to provide for complete destruction of the film base, in order to prevent retrieval of classified information, from the image or the latent image often present as an integral part of the film base.

It is an object of this invention to provide a procedure for processing developed and/or undeveloped silver emulsion coated organic substrates for the recovery of silver and organic by-products, in which the process is characterized by:

1. complete recovery of substantially all of the silver;
2. treatment of bulk material without manual or mechanical pre-processing to minimize cost;
3. yield of a refined or easily refined silver; 4. rapid processing to minimize silver inventory;
5. minimum environmental impact;

6. recovery of marketable by-products from the organic film substrate; and

7. decomposition of the substrate material and emulsion to preclude retrieval of images or latent images retained thereon.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, a flow diagram is submitted herewith as representative of a process embodying the features of this invention.

Briefly described, in accordance with the practice of this invention, silver emulsion coating, developed and/or undeveloped, and the organic film base, such as triacetate, Mylar (terephthalate acid esters) etc., are placed in an autoclave together with sufficient amount of silver complexing agent, such as ammonium hydroxide, to form a complex compound with the silver that is present, such as to form a silver amine complex when use is made of ammonia.

Sufficient excess of the ammonium hydroxide is provided to insure that the organic depolymerization products of the film base are formed as their corresponding soluble amine, amide, or the like soluble nitrogen containing organic compounds resulting from the reaction between the film material of the film base and the ammonium hydroxide.

The mixture of silver emulsion coated film base, water and complexing agent is subjected to wet oxidation at a temperature above about 400°F but less than 500°F, and at elevated pressure such as within the range of 500 to 1000 p.s.i.g. and preferably 650 to 1,000 p.s.i.g., in the presence of oxygen containing gas, such as oxygen or air. The oxygen in the form of oxygen, air or other oxygen containing gas is incorporated in a ratio within the range of 0.2 to 1 of the theoretical chemical oxygen demand (COD) of the organic material that is present. The mixture of film, water and complexing agent is agitated sufficiently to insure that the rate of oxygen dissolution in the liquid phase is not rate-limiting to the wet oxidation of the materials which are suspended or dispersed in the aqueous liquor. In the preferred practice of this invention, when use is made of ammonium hydroxide as the complexing agent, the wet oxidation reaction is carried out at a temperature preferably within the range of 460°-465°F, with an oxygen/COD ratio of 0.7 to 0.85, with the ammonia 1.5 to 2 times the amount required to form an amine complex with the silver present, all of which can be calculated in advance from the known composition of the film material to be processed.

The wet oxidation reaction is markedly enhanced by the presence of a catalyst. For this purpose, use can be made of salts which provide free ions of copper, silver, and ammonia in the amount within the range of  $10^{-2}$  to  $10^{-4}$  moles per liter, when calculated on the basis of copper sulphate. The silver catalyst can be supplied from the dissolution of silver during the wet oxidation reaction or by the addition of silver salt, such as silver sulphate.

When calculated on the basis of ammonium sulphate as the preferred source of the ammonium ion, the amount of ammonium sulphate added to the mixture for the wet oxidation reaction should be within the range of 75-150 grams per liter. There is reason to believe, from the observations which have been made, that the added ammonium sulphate also functions as an effective wet oxidation catalyst, such observations being predicated on batch experiments in which 30-40

grams of chopped film has been subjected to wet oxidation under the conditions described.

Upon completion of the wet oxidation reaction, all of the materials present appear to be in solution except for small or trace amounts of solids which can be separated out as inert material or else recycled for additional wet oxidation in the next batch. The liquor can be used again and again in the wet oxidation of additional emulsion coated film until the concentration of materials builds up to a level for efficient removal of products resulting from the wet oxidation, thereby to provide considerable savings in processing steps, formulation, and utilization of chemicals. In the alternative, the product from the wet oxidation step can be subjected directly to processing for the removal or recovery of various of the valuable components in solution therein.

Having described the basic concepts of this invention, an example of the practice of the invention will hereinafter be given by way of illustration, but not by way of limitation.

30.8 grams of undeveloped photographic film, containing 1.14% silver concentrated in the silver emulsion, on a Mylar base, was chopped into small pieces and introduced along with 150 grams of ammonium sulphate,  $10^{-3}$  moles of copper sulphate and water in an amount to make up 1.5 liters, into a reactor of the type described in our copending applications, Ser. No. 400,123, now U.S. Pat. No. 3,870,631 and Ser. No. 403,652, now U.S. Pat. No. 3,852,192. The wet oxidation reactor, in the form of an autoclave, for high pressure operation, is provided with a high speed stirrer and inlets for the introduction of air at or near the vortex of the stirrer for immediate and uniform distribution of the air as fine particles throughout the liquor for maximum dissolution of oxygen therein. The wet oxidation was carried out with the constant introduction of air, and constant stirring, with the liquor maintained at a temperature of 460°F and under 1,000 psig until dissolution of the material was substantially complete, or for about one to two hours. The COD of the effluent was calculated as 812 mg/l-0.

The effluent was recycled to the wet oxidation reactor with 32.8 grams of chopped film introduced into the reactor as a second charge. The reactor was operated in the same manner as before, except that a pressure of 970 psig was used. The effluent from the wet oxidation of the second batch had a COD of 685 mg/l-0.

The liquor effluent from the second batch was recycled for a second time for wet oxidation of an additional 32.5 grams of chopped film at 461°F and 1,035 psig. The effluent liquor, having a COD of 869 mg/l-0 was recycled for the third time for wet oxidation with an additional increment of 34.9 grams film, at 460°F and 695 psig. The final liquid phase, identified in the flow diagram as pregnant complex silver solution, had a COD of 897 mg/l-0.

The final effluent contained 1,246 grams per liter of silver.

The silver can be recovered from the pregnant complex silver solution or leach liquor by a number of ways, including:

1. the addition of sulphuric acid to produce silver sulphate which precipitates and can be separated by conventional water-solid separation techniques;

2. the addition of nitric acid to convert the silver amine complex to silver nitrate in accordance with the process described by D. M. Liddell, Handbook of Non-

Ferrous Metallurgy, Recovery of the Metals, Chapter X, p. 275, McGraw-Hill Publishing Company, followed by electrowinning as by the Moebius process;

3. by hydrogen reduction of silver chloride precipitated from the silver amine solution by the introduction of chloride ion;

4. by direct hydrogen reduction of the silver amine complex solution with gaseous hydrogen under high temperature and pressure;

5. by direct reduction of the silver from solution by such reducing compounds as glucose and formaldehyde.

In the example described, direct reduction with hydrogen was used by introduction of hydrogen under high pressure in the same reactor or autoclave used to carry out the high pressure, high temperature wet oxidation. Reduction with hydrogen was carried out at a temperature of 420°-500°F under a pressure within the range of 700 to 1,000 psig. The freed silver precipitated and was recovered from the liquor by filtration, centrifugation, decantation, or the like liquid-solid separation techniques.

After removal of the silver, the remaining leach liquor contains the terephthalate derived from the Mylar film base, in the form of the amine or amide. The liquor is acidified, as with a mineral acid such as nitric or sulphuric acid to a pH within the range of 2 to 5 to form terephthalic acid which separates out as a precipitate. It is preferred to make use of nitric acid for acidification, since any trace quantities of silver will then be retained in solution for recycling with a new batch of pregnant complex silver solution.

It will be apparent from the foregoing that we have provided a process which, in the first place, operates efficiently and effectively to destroy imaged or unimaged photosensitive film, and which operates effectively and efficiently to convert the film materials into a form from which the silver can be recovered in a usable form and from which the organic materials derived from the film base can be recovered in a useful form.

It will be understood that changes may be made in the details of formulation and operation, without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A process for the destruction of developed or undeveloped film having a silver emulsion coating comprising the steps of mixing the film with an aqueous medium containing an agent which forms a soluble complex with silver, subjecting the mixture to wet oxidation at elevated temperature and elevated pressure while introducing an oxygen containing gas under a high state of agitation for rapid distribution of the oxygen into the liquid mixture, continuing the wet oxidation reaction until the chemical oxygen demand COD of the organic material in the mixture is reduced and the silver and film material are converted to a soluble state within the resulting liquor, and treating the liquor to separate the silver.

2. A process as claimed in claim 1, in which the wet oxidation reaction is carried out in the presence of a wet oxidation catalyst.

3. The process as claimed in claim 2 in which the catalyst is selected from the group consisting of ions of copper, silver and ammonium.

4. The process as claimed in claim 3 in which, when the catalyst is copper ion, the ions are present in an

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amount within the range of  $10^{-3}$  to  $10^{-4}$  moles per liter when calculated on the basis of copper sulphate.

5. The process as claimed in claim 3 in which the copper, silver and ammonium ions are provided in the form of the sulphates of copper, silver and ammonium.

6. The process as claimed in claim 1 in which the agent which forms a soluble complex with the silver is a complex which forms a silver amine or amide complex.

7. The process as claimed in claim 6 in which the complexing compound is in the form of an ammonium ion.

8. The process as claimed in claim 7 in which the ammonium complexing compound is selected from the group consisting of ammonium hydroxide and ammonium sulphate.

9. The process as claimed in claim 6 in which the complexing compound is present in an amount within the range of 1.5 to 2 times the amount required to form the complex with the amount of silver that is present.

10. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a temperature within the range of 400°-500°F.

11. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a temperature within the range of 460°-465°F.

12. The process as claimed in claim 9 in which, when the complexing agent is present in the form of ammonium hydroxide, the wet oxidation reaction is carried out at a temperature within the range of 460°-465°F, and at a pressure within the range of 500-1000 psig.

13. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a pressure within the range of 500-1000 psig.

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14. The process as claimed in claim 1 in which the wet oxidation reaction is carried out at a pressure within the range of 650-1000 psig.

15. The process as claimed in claim 1 in which the oxygen containing gas is air.

16. The process as claimed in claim 1 in which the oxygen is introduced in an amount to provide an oxygen/COD ratio of 0.2 to 1.0.

17. The process as claimed in claim 1 in which the oxygen containing gas is introduced into the aqueous liquid in the immediate vicinity of the vortex of the agitator.

18. The process as claimed in claim 1 in which the solubilized silver in the liquor resulting from the wet oxidation is separated by the addition of nitric acid to convert the silver ions to silver nitrate, and then electro-winning the silver from the silver nitrate solution.

19. The process as claimed in claim 1 in which the liquor remaining from the wet oxidation step is recycled with additional emulsion coated film through a subsequent wet oxidation step until the amount of dissolved material rises to levels suitable for the subsequent separation step.

20. A process for the destruction of photosensitive film (developed or undeveloped) and the recovery of products therefrom comprising the steps of mixing the film with an aqueous medium for suspension or dispersion of the film in the aqueous medium, subjecting the mixture to wet oxidation at elevated temperature and at elevated pressure, while introducing an oxygen containing gas under a high state of agitation for substantially immediate dissolution of the oxygen in the liquid mixture, and continuing the wet oxidation reaction until the film materials are substantially converted to a soluble state within the liquor, and then processing the resultant liquor to separate out various of the components derived from the destruction of the film.

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## Project Summary

# Wet Oxidation and Ozonation of Specific Organic Pollutants

C. Robert Baillod and Bonnie M. Faith

This study was undertaken to assess the applicability of wet oxidation and ozonation to the treatment of wastewater containing five specific pollutants typical of the 114 organic compounds included on the EPA priority pollutant list. The pollutants, phenol; 2-chlorophenol; 4-nitrophenol; 1,2-dimethylphthalate and 1,2-dichloroethane were selected for study on the basis of their occurrence, structure, water solubility, and volatility. The ability of the wet oxidation and ozonation processes to oxidize these pollutants in aqueous solution was studied using batch laboratory-scale experiments. In the case of wet oxidation, efforts were made to determine the influence of temperature, pH value, catalyst, and reaction time on the degree of pollutant destruction. In addition, an economic evaluation was made of a wet oxidation process designed to treat a refractory petrochemical waste stream. For ozonation, information was developed on the degree of pollutant destruction as influenced by ozone dosage and contact time. For both processes, the fate of pollutants were studied by measuring products of incomplete oxidation. The ozonation results showed that 1,2-dichloroethane was rapidly volatilized and the remaining four pollutants could be removed to less than detectable concentrations, in 5 to 10 minutes, at initial ozone usage rates of 3.9 to 5.9 moles of ozone per mole of compound removed. The wet oxidation results indicate that all five pollutants could be oxidized under the conditions of temperature (204° C to 260° C) and oxygen pressures studied. The removal rates for each substance depended on temperature, pH, and catalyst and were adequately described by semi-empirical, first-order kinetics. For both processes,

a significant amount of organic carbon remained in solution after the specific pollutants had been removed. This carbon was slowly oxidized and consisted primarily of organic acids and aldehydes. A wet oxidation process was designed to treat a 37.8 l/min (10 gal/min) of a high COD (70,000 mg/l) petrochemical waste which was inhibitory to a biological treatment process. A detailed economic evaluation of this process indicated that an investor's interest rate of 20 percent could be attained at a treatment charge of \$69 per 1000 gallons (\$17.81 per cubic meter) or \$0.16 per pound of COD removed (\$0.35 per Kg COD removed).

*This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Experimental Results

Semi-batch ozonation experiments showed that:

Phenol, 2-chlorophenol, 4-nitrophenol and 1,2-dimethylphthalate could be removed to less than detectable concentrations (in 5 to 10 minutes) through ozonation at initial ozone utilization ratios of 3.9 to 5.9 moles of ozone per mole of specific pollutant. However, the removal rates were limited by the rate of ozone mass transfer. During the initial stages of the ozonation experiments, reaction in the diffusive film enhanced the mass transfer rate.

A significant amount of total organic carbon remained in solution after the specific pollutants had been removed

and this carbon was slowly oxidized. Increasing the initial pH from 6 to 10: a) increased the specific pollutant removal rate for phenol and 4-nitrophenol, but decreased the rate for 2-chlorophenol, and b) decreased the total organic carbon removal rates for phenol and 2-chlorophenol.

Batch wet oxidation experiments showed that:

All five specific pollutants studied could be oxidized under the conditions of temperature and oxygen pressured studied. The removal rates depended on the substances and on temperature and were adequately described by semi-empirical first-order kinetics.

Alkaline pH levels markedly increased the rate of specific pollutant removal and only slightly increased the rate of total organic carbon removal. However, over the one-hour reaction period, alkaline pH levels gave markedly lower removals for total organic carbon and chemical oxygen demand.

Cupric ion acted as a catalyst and increased the rate and extent of removal of specific pollutants and total organic carbon.

A significant amount of total organic carbon remained in solution after the specific pollutants had been removed and this carbon was slowly oxidized. More than three-fourths of this carbon was accounted for by low molecular weight acids, acetaldehyde and acetone.

Bioassay tests using *Daphnia magna* indicated that wet oxidation achieved 90 to 99 percent detoxification for phenol, 2-chlorophenol and 4-nitrophenol.

Although acetic acid was a major end

evident during ozonation. Conversely, oxalic acid was a relatively minor product during wet oxidation, but was very significant in ozonation.

*C. Robert Baillod and Bonnie M. Faith are with Michigan Technological University, Houghton, MI 49931.*

*Ronald J. Turner is the EPA Project Officer (see below).*

*The complete report, entitled "Wet Oxidation and Ozonation of Specific Organic Pollutants," (Order No. PB 83-254 060; Cost: \$16.00, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:  
Industrial Environmental Research Laboratory  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268*

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: JEPLO108529  
: ROBERT C BAILLOD  
: MICHIGAN TECH  
: CIVIL ENGR DEPT  
: ASSOC PROFESSOR  
: HOUGHTON MI 49931

APPENDIX D  
MTU KEY PERSONNEL

C. ROBERT BAILLOD  
October 1983

PERSONAL INFORMATION

C. Robert BailloD, Professor of Civil and Environmental Engineering and  
Director, Water and Waste Management Group of BioSource  
Michigan Technological University  
Houghton, Michigan 49931  
(906) 487-2530

Birthdate: *non-responsive*

Place of Birth: *non-responsive*

Home Address: *Non-responsive*  
*Non-responsive*  
*- Non-responsive*

EDUCATION

1963, B.S. - Civil Engineering  
Marquette University, Milwaukee, Wisconsin

1965, M.S. - Civil Engineering  
University of Wisconsin, Madison, Wisconsin  
Major Area of Study - Environmental Engineering

1968, Ph.D.  
University of Wisconsin, Madison, Wisconsin  
Major Area of Study - Environmental Engineering

HONORS

Graduated Cum Laude, B.S.C.E. (1963)

Corecipient: Michigan Society of Prof. Engineers Outstanding Achievement in  
Engineering Education Award, 1981

Tau Beta Pi, Chi Epsilon, Sigma Xi

Registered Professional Engineer in Michigan and Wisconsin

EXPERIENCE

1982 to Present, Professor of Civil and Environmental Engineering and Director  
of the Water and Waste Management Group of BIOSOURCE  
Michigan Technological University  
Duties: Approximately 60% Academic Teaching, Research and Administration:

Environmental Engineering Group Leader. 40% BioSource: Supervision of two research engineers, technician and secretary; budget management; Coordinator of Faculty research efforts, Wet Oxidation and Oxygen Transfer Research Group Leader

1983- Sabbatical, Spring Semester, Visiting Professor, Rogaland Districthogskole, Stavanger, Norway

1978 to 1982, Professor of Civil and Environmental Engineering  
Co-Director, Center for Waste Management Programs  
Michigan Technological University

Responsibilities: Teaching undergraduate and graduate courses; supervision of graduate research; Environmental Engineering Area Leader

1977 to 1978, Visiting Professor  
Department of Civil and Environmental Engineering  
University of Wisconsin, Madison, Wisconsin

1968 to 1978, Assistant and Associate Professor  
Department of Civil Engineering  
Michigan Technological University

1968, Project Engineer  
University of Wisconsin Experiment Station  
Responsibilities: Influence on Turbulence on Oil-Water Separation

1965 to 1968, Federal Water Pollution Control Administration Research Fellow  
Department of Civil Engineering  
University of Wisconsin, Madison, Wisconsin

1964 to 1968, National Science Foundation Trainee  
Department of Civil Engineering  
University of Wisconsin, Madison, Wisconsin

1963 to 1964, Engineer I  
Wisconsin Department of Transportation

#### MAJOR RESEARCH SPECIALTIES

Biological treatment processes, removal and fate of toxic pollutants, oxygen transfer, wet oxidation.

#### RESEARCH PROJECTS

Michigan Technological University Faculty Research Grants, 1969-1970  
"Aerobic Sludge Digestion - Land Disposal of Municipal Effluents"  
\$2,100

Michigan State University, 1969-1971  
Institute for Water Research, East Lansing, Michigan  
"Nitrification in Surface Waters"  
\$7,292



U.S. Environmental Protection Agency and Cleveland Cliffs Iron Company, 1970-1973  
"Storage and Disposal of Waste Water Resulting from the Concentration of Low  
Grade Iron Ore"  
\$73,603

U.S. Army Cold Regions Research and Engineering Laboratory, 1976  
"Continued Evaluation of the Calumet, Michigan Land Application Waste Water  
Treatment Site"  
\$2,500

U.S. Army Cold Regions Research and Engineering Laboratory, 1975  
"Preliminary Evaluation of the Calumet, Michigan Land Application Waste Water  
Treatment Site"  
\$2,500

Michigan Technological University Faculty Research Grant, 1977-1978  
"A Study of Wet Oxidation and Heat Treatment of Sewage Sludge and Hazardous  
Waste"  
\$2,200

U.S. Environmental Protection Agency, 1978-1980  
"Development of a Tentative Standard for Evaluating Oxygen Transfer"  
\$70,000 (Member of ASCE Task Group)

U.S. Environmental Protection Agency, 1978-1980  
"Utility of Wet Oxidation and Ozonation in the Treatment of Priority Organic  
Pollutants"  
\$193,000

U.S. Environmental Protection Agency, 1981-1983  
"Evaluation of Oxygen Transfer Test Procedures"  
\$250,000 (Member of ASCE Task Group)

Lakeside Equipment Corp., 1982-83  
"A Study of Computer Aided Design Applied to the Oxidation Ditch Process"  
\$4,000

Hazen Research Inc., 1983  
"Wet Oxidation of Dioxin Surrogates"  
\$10,000

#### PROFESSIONAL MEMBERSHIPS AND SOCIETY ACTIVITIES

American Society of Civil Engineers, Member  
Journal of the Environmental Engineering Division, Referee  
National Subcommittee on Oxygen Transfer Standards (1978- )  
ASCE-EPA Oxygen Transfer Task Force (1978- )  
Association of Environmental Engineering Professors, Member  
Membership Committee, 1975  
American Water Works Association  
Michigan Education Committee 1977-82  
Trustee, Michigan Section 1978-81  
Water Pollution Control Federation, Member  
Joint Task Force on the 16th Edition of Standard Methods (1979- )

PUBLICATIONS

1. Balllod, C.R. and B.M. Faith, "Wet Oxidation and Ozonation of Specific Pollutants," EPA Project Summary Report, EPA 600/S2-83-060, August, 1983.
2. Bettinger, J.E., C.R. Balllod and R.A. Lamparter, "Peat Combustion and Enhancement by Wet Oxidation," Chem. Engr. Progress, (In press) 1983.
3. Balllod, C.R. and L.C. Brown, Section 4 "Modeling and Data Interpretation," In Development of Standard Procedures for Evaluating Oxygen Transfer Devices published by U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, available from N.T.I.S., Aug., 1983, pages 11-55.
4. Balllod, C.R., "Proposed Standard for Measurement of Oxygen Transfer in Clean Water," proceedings, Conference on Aeration System Design Testing and Control, U.S.E.P.A. and Environmental Canada, August, 1982, 47 pages.
5. Balllod, C.R. and B.M. Faith, "Wet Oxidation and Ozonation of Specific Organic Pollutants," published by U.S. Environmental Protection Agency, EPA 600/2-83-060, available from N.T.I.S., Aug., 1983, 142 pages.
6. Balllod, C.R., B.M. Faith and O. Masl, "Wet Oxidation and Ozonation of Specific Pollutants," Environmental Progress 1(3):217-227, 1982.
7. Brown, L.C. and C.R. Balllod, "Modeling and Interpretation of Oxygen Transfer Data," Jour. Env. Engr. Div. ASCE 108(EE4):607-628, 1982.
8. Skaates, J.M., B.A. Griggs, R.A. Lamparter and C.R. Balllod, "Wet Oxidation of Glucose," Canadian Journal of Chemical Engineering, 59:517-521, 1981.
9. Balllod, C.R., "Review of Oxygen Transfer Model Refinements and Data Interpretation," Proceedings, Workshop toward an Oxygen Transfer Standard, EPA 600/9-78-021, p. 17-26, 1979.
10. Balllod, C.R., Cressey, G.M. and Beaupre, R.T., "Influence of Phosphorus Removal on the Solids Budget at a 1.7 MGD Activated Sludge Plant with Aerobic Digestion," Journal of the Water Pollution Control Federation, 49:131-145, January, 1977.
11. Balllod, C.R., R.G. Waters, I.K. Iskandar and A. Ulga, "Preliminary Evaluation of 88 years Rapid Infiltration of Raw Municipal Sewage at Calumet, Michigan," In Land as a Waste Management Alternative, Ed. by R.C. Loehr, Ann Arbor Science Press, 489-510, 1977.
12. Balllod, C.R., R.A. Lamparter and D.G. Leddy, "Wet Oxidation of Toxic Organic Substances" Proceedings-Control of Specific Pollutants, Air Pollution Control Association, p. 232-245, 1979.
13. Balllod, C.R., R.A. Lamparter and D.G. Leddy, "Wet Oxidation of Toxic Organic Substances" Proceedings, Purdue Ind. Waste Conference, Ann Arbor Science, 206-213, 1979.

14. Baillod, C.R. and G.R. Alger, "Storage and Disposal of Iron Ore Processing Waste Water," U.S. Environmental Protection Agency, Publication No. EPA-660/2-74-018, March, 1974.
15. Alger, G.R. and C.R. Baillod, "Mine Tailings Basins and their Associated Watersheds," In Watersheds In Transition, Ed. by S.C. Csallany, American Water Resources Association, Minneapolis, 1972.
16. Baillod, C.R. and F.B. Christensen, "Hydraulic and Sedimentation Efficiencies of Tailings Clarification Basins," Proceedings, 27th Industrial Waste Conference, Engineering Bulletin of Purdue University, Engineering Extension Series No. 141, 1972, pp. 727-746.
17. Baillod, C.R. and W.C. Boyle, "Mass Transfer Limitations in Substrate Removal," Journal of the Sanitary Engineering Division, Proceedings, ASCE, April, 1970, SA-2, pp. 525-545.
18. Baillod, C.R., G.R. Alger and H.S. Santeford, "Wastewater Resulting from the Concentration of Low Grade Iron Ore," Water and Sewage Works, October, 1970, p. 359-364.
19. Baillod, C.R. and W.C. Boyle, "Instrument Response Time in an Analytical System for Continuous Glucose Measurement," Environmental Science and Technology, 3:1205, 1969.
20. Baillod, C.R. and W.C. Boyle, "An Experimental Valuation of the Intra-Particle Resistance in Substrate Transfer to Suspended Zoogloal Particles," Proceedings, 24th Industrial Waste Conference, Engineering Bulletin of Purdue University, Engineering Extension Series No. 135, pp. 302-326, 1969.
21. Baillod, C.R. and W.C. Boyle, "Activated Sludge Nitrification in the Presence of Linear and Branched-Chain Alkyl Benzene Sulfonates," Applied Microbiology, 16:62, 1968.
22. "Sanitary Engineering," In Emerging Techniques in Civil Engineering Education, A.S.C.E., June, 1973, p. 22.
23. "Nitrification in Surface Waters," Water Resources Research Catalog, Volume 5, p. 1-443, 1969.
24. "Storage and Disposal of Wastes Resulting from the Concentration of Low Grade Iron Ore," Water Resources Research Catalog, Volume 6, 1970.
25. "An Analysis of Mass Transfer Limitations of Substrate Removal by Biological Floc Particles," ASCE Second National Symposium on Sanitary Engineering Research and Design, p. 33, 1969, abstract.
26. Baillod, C.R., "Mass Transfer of Glucose through Bacterial Floc," Ph.D. Thesis, Univ. of Wisconsin, 1968.
27. Baillod, C.R., "Effects of Anionic Detergents on Nitrification in Activated Sludge," M.S. Thesis, Univ. of Wisconsin, 1965.

## TEACHING PUBLICATIONS

1. Baillod, C.R., "Notes on Hydraulic Engineering with Applications to Water Supply and Sewerage," MTU Civil Engineering Department, 1976, 147 pages.
2. Baillod, C.R., "Notes on Environmental Engineering," 5th Edition, MTU Civil Engineering Department, 1975, 266 pages.
3. Baillod, C.R., ed., "Environmental Engineering Laboratory Manual," MTU Civil Engineering Department, 1979, 132 pages.

## PRESENTATIONS

1. Baillod, C.R., L.C. Regenmorter and R.A. Lamparter, "A Mathematical Model of a Wet Oxidation System for the Treatment of Aqueous Organic Residuals," Presented at the AIChE National Meeting, Houston, 1983.
2. Paulson, W.L. and C.R. Baillod, "A Proposal Standard for Management of Oxygen Transfer Rate in Clean Water," Presented at the E.P.A. Environment Canada Conference on Aeration System Design, Operation, Testing and Control, Madison, Wisconsin, August 2-4, 1982.
3. Bettlinger, J.A., C.R. Baillod and R.A. Lamparter, "Peat Combustion and Enhancement by Wet Oxidation," Presented at the American Institute of Chemical Engineers, Spring Meeting, Houston, Texas, April, 1983.
4. Baillod, C.R., "Interpretation of Oxygen Transfer Data." Lecture presented at the University of Aalborg, Aalborg, Denmark, April 15, 1983.
5. Baillod, C.R., "Oxygen Transfer Data Analysis." Seminar presented at the Technical University of Braunschweig, Braunschweig, Germany, April 18, 1983.
6. Baillod, C.R., "Measurement and Interpretation of Oxygenation Capacity." Lecture presented to engineers from 40 nations at the International Institute for Hydraulic and Environmental Engineering, Delft University of Technology, Delft, Netherlands, April 22, 1983.
7. Baillod, C.R., "Removal of Toxic Pollutants from Wastewater," Presented at the 3rd Annual Symposium on Hazardous Waste Management, Michigan Technological University, June 17-18, 1982.
8. Baillod, C.R., "Sludge Production and Material Balances" and "Thermochemistry and Energy Balances in Sludge Combustion," Presented at the Workshop on Wastewater Sludge Management Facilities, University of Wisconsin, Madison, July 15-17, 1981.
9. Baillod, C.R., B.M. Faith and O. Masi, "Wet Oxidation and Ozonation of Specific Pollutants," Presented at the National Conference of the AIChE, New Orleans, Nov., 1981.
10. Brown, L.C. and C.R. Baillod, "Modelling and Interpretation of Unsteady-State Oxygen Transfer Data," Presented at the National Environmental Engineering Conference, ASCE, New York, July, 1980.

11. Baillod, C.R., "Treatment of Toxic Wastewaters and Sludges," Presented at the Second Annual M.T.U. Symposium on Toxic and Hazardous Wastes, June, 1980.
12. Baillod, C.R., "Theory of Oxygen Transfer Testing," Presented at the Conference on Design Testing and Control of Oxygen Transfer Systems, University of Wisconsin, Madison, March 9-11, 1981.
13. Baillod, C.R., "Sludge Sources, Sinks and Material Balances," Presented at the Conference on Wastewater Sludge Management Facilities, University of Wisconsin, Madison, July 29-31, 1980.
14. Baillod, C.R., "Dissolved Air Flotation," Presented at the Conference on Wastewater Sludge Management Facilities, University of Wisconsin, Madison, July 29-31, 1980.
15. Baillod, C.R., "Aerobic Digestion and Composting," Presented at the Conference on Wastewater Sludge Management Facilities, University of Wisconsin, Madison, July 29-31, 1980.
16. Baillod, C.R., "Sludge Dewatering," Presented at the Conference on Wastewater Sludge Management Facilities, University of Wisconsin, Madison, July 29-31, 1980.
17. Baillod, C.R., "Rapid Infiltration Systems: Case Study and Design Considerations," Presented at the Conference on Land Treatment of Wastewater, University of Wisconsin, Madison, December 9-11, 1980.
18. Baillod, C.R., R.A. Lamparter and D.G. Leddy, "Wet Oxidation of Toxic Organic Substances," Presented at the 34th Purdue University Industrial Waste Conference, Lafayette, Indiana, May, 1979.
19. Baillod, C.R. and L.C. Brown, "Standard Method for the Evaluation of Oxygen Transfer: Modeling and Data Analysis, Final Draft," Presented at the Summary Wrap-up Meeting of the ASCE Subcommittee, San Diego, CA, November, 1979.
20. Baillod, C.R., "Design of Rapid Infiltration Systems," Presented at the Conference on Land Treatment of Wastewater, Madison, WI, November, 1979.
21. Baillod, C.R., "Design of Coagulation, Flocculation and Adsorption Systems," Presented at the Conference on Physical-Chemical Treatment of Wastewater, Madison, WI, December, 1979.
22. Baillod, C.R., "Removal of Specific Pollutants from Wastewater," Ultimate Disposal of Toxic Pollutants," Presented at the M.T.U.-C.W.M.P. Symposium of Toxic and Hazardous Wastes, June, 1979.
23. Baillod, C.R., D.G. Leddy and R.A. Lamparter, "Destruction of Organic Substances by Wet Oxidation," Presented at the Conference on Control of Specific Toxic Pollutants, Gainesville, Florida, February, 1979.

RICHARD A. LAMPARTER

PERSONAL INFORMATION

Richard A. Lamparter, Senior Research Engineer  
BioSource Institute  
Michigan Technological University  
Houghton, Michigan 49931

Home Address:

*Non-Responsive*  
*Non-Responsive*  
*Non-Responsive*

EDUCATION

1959, B.S. Chemical Engineering  
Wayne State University, Detroit, Michigan

EXPERIENCE

1977 to Present, Senior Research Engineer  
Michigan Technological University, Houghton, Michigan  
Responsibilities - direction of the set-up of laboratory test equipment; coordination of efforts for procurement and establishment of pilot plant test equipment; establishment of laboratory building and test facility requirements; principal investigator on contracts for "Coal Combustion by Wet Oxidation," "Recovery of Clay from Paper Wastes," and "Reclamation of activated carbon used in Biological Treatment Ponds"; direction of research programs in the areas of waste treatment, resource recovery, and energy recovery.

1971 to 1977, Waste Treatment Engineer  
Lockheed Missiles and Space Company, Inc.  
Responsibilities - involved in Lockheed's development of wet oxidation waste treatment systems since 1971; process analysis toward the objective of selecting optimum operating parameters, including the evaluation of catalysts, set-up of test procedures, and the coordination of chemical analysis, prepared proposals for wet oxidation waste treatment systems for government and industrial waste waters, coordinated waste evaluation research with industrial clients including evaluation of plant waste sources to define special treatment problems, developed computer programs for the economic and system analysis of the wet oxidation process. Recently served as consultant in the development of the two phase heat exchanger and reactor analysis programs, augmented wet oxidation product line through development work on activated carbon, precipitation, filtration, and chemical treatment techniques. Other areas of waste treatment include development of a complete preliminary design of a process for the disposal of sodium sludge; project leader on research of an electrochemical process for treatment of human wastes, evaluation of techniques for restoring waste water to potable standards on spacecraft. Air pollution-involved in projects for maintaining a habitable environment since 1966. Work has been directed toward developing generalized design

correlations and systems analysis.

1966 to 1971, Life Support Engineer  
Lockheed Missiles and Space Company, Inc.

1959 to 1966, Analytical Engineer  
Hamilton Standard Division  
United Aircraft Corporation

#### RESEARCH PROJECTS

Manistique Pulp and Paper Company  
December 1978 to June 1979  
Manistique, Michigan  
"Recovery of Clay from a Paper Recycle Stream"

AMOCO Research Corporation,  
October 1978 to January 1980  
Chicago, Illinois  
"Activated Carbon Regeneration"

Department of Energy  
October 1978 to October 1980  
"Development of a Process for Recovery of Energy from Wet Oxidation of Coal"

AMOCO Research Corporation  
September 1979 to January 1980  
Chicago, Illinois  
"Treatment of an Oil Shale Process Waste Water"

#### Publications and Presentations

- X 1. Bettinger, J.A., Balllod, C.R., Lamparter, R.A., "Peat Combustion and Enhancement by Wet Oxidation," AIChE Spring Meeting, March 27-31, 1983.
- X 2. Balllod, C.R., Regenmorter, L.C., Lamparter, R.A., "A Mathematical Model of a Wet Oxidation System for Treatment of Aqueous Organic Residuals," AIChE Spring Meeting, March 27-31, 1983.
- X 3. Brady, W.P., Barna, B.A., Lamparter, R.A., "Solvent Pulping by HMDA Extraction of Lignin Offers Potential for High Yield High Quality Pulp," Tappi-1981 Pulping Conference.
- ck 4. Barna, B.A., Johnsrud, D.R., Lamparter, R.A., "Petrochemicals from Waste: Recycling PET Bottles," Chemical Engineering, December 1, 1980.
- X 5. Bettinger, J.A., Lamparter R. A., McDowell D.C., "Coal Combustion by Wet Oxidation" DOE/ET/12328-T2, November 15, 1980
- X 6. Balllod, C.R., Lamparter, R.A., Leddy, D.G., "Wet Oxidation of Toxic Organic Substances," Purdue Industrial Waste Conference, May, 1979
- ✓ 7. Jagow, R.B., Lamparter, R.A., Katan, T., Ray, C.D., "Investigation of Low Temperature Carbon Monoxide Oxidation Catalysts," ASME Publication 77-ENAS-28

8. Olcott, T.M., Lamparter, R.A., "Estimating Sorber Capacity for Multiple Containments," NASA Tech Brief, December 1973
9. Lamparter, R.A., "Development of Zero Gravity Hydrophobic Hydrophilic Bubble Separators," NASA CR-66922, May 18, 1970
- X 10. Olcott, T.M., Lamparter, R.A., "Evaluation Testing of a Zero Gravity Humidity Control System," NASA CR-66543, October 25, 1967
11. Lamparter, R.A., "Study and Preliminary Design of an Isotope Heated Catalytic Oxidizer System," NASA, CR-66497



APPENDIX E  
PROPOSED PROCESS DESCRIPTION

## INTRODUCTION

The proposed process which can solve the contaminated film chip problem is based on Michigan Technological University (MTU) patents of "Process for the Destruction of Developed and Undeveloped Photosensitive Film and the Recovery of Products Therefrom". In the process the polyethylene terephthalate (PET) film is broken down into its formative constituents of terephthalic acid and ethylene glycol. The silver and terephthalic acid are recovered as valuable products from the process.

The process is related to and is an outgrowth of wet air oxidation technology which has a proven record of destroying hazardous materials.

MTU and others have shown that wet air oxidation and the proposed film process which are related are capable of destroying in excess of 99.5 percent of the total cyanide. The only products of this destruction are carbon dioxide and ammonia. The cyanide concentration in the process waste liquor will be below .5 parts per million (ppm) and usually below .2ppm.

As the process is a wet combustion process, other contaminants such as paper, wood, and non PET film will be broken down and oxidized. Thus, if contaminants are held to levels at or below those already tested, product quality will not be compromised. High contamination levels, currently unknown, may reduce the quality of the product terephthalic acid.

The process has been demonstrated in a pilot plant capable of recycling up to 150,000 pounds per month of x-ray film. Samples of the cyanide tainted scrap film have been processed in a small laboratory reactor to show cyanide destruction and to provide data on product terephthalic acid quality. Thus, the element of project risk has been minimized.

## CHEMICAL BASIS

PET, the main constituent of the scrap film pile is a polymer made from terephthalic acid and ethylene glycol alternating in a chain. When these materials are reacted, eliminating water between them, they form the polymer (plastic) film. Under conditions of moderate temperature and pressure (450°F and 650 psia) in the presence of water in an autoclave, the polymer chain is broken and the starting resources

recovered. The MTU patented process causes this breakdown (depolymerization) to occur in the presence of a strong base such as sodium hydroxide. The terephthalic group forms a soluble sodium salt of terephthalic acid which goes into solution with the ethylene glycol formed.

The solution leaving the reactor will have film contaminants which entered with scrap film such as dirt, stones and in the case of untreated film silver as the only solids in suspension. These solids are removed in a filter for disposal or recovery of silver. The clear solution leaving the filter contains primarily the sodium terephthalate, ethylene glycol and a minor quantity of excess sodium hydroxide.

When the filtered solution is treated with an inexpensive acid, such as sulfuric acid, an exchange will occur forming sodium sulfate which is soluble and terephthalic acid which is insoluble. The terephthalic acid can then be separated by filtration, dried, and sold to make new film.

The ethylene glycol and sodium sulfate are best discharged to a waste treatment system as their recovery would not be economical. Tests carried out on film chip process waste water have shown it to be biodegradable. No adverse environmental effects associated with the discharge will be encountered.

As the process is similar to wet oxidation, most of the film contaminants will be oxidized to carbon dioxide, water, and low molecular weight organic acids. Fortunately, the terephthalic acid and ethylene glycol, are not altered in the environment. Thus, most contaminants will not present a problem.

As a wide range of contaminants and products are anticipated, and as it is not possible to predict the mix in advance, an assumption was made in which half of the combustibles were converted to carbon dioxide and water and the balance to acetic acid. A mass balance summary was then prepared for each 100 lbs. of film processed. This summary (enclosed) shows the flows into and out of each of the principal process steps. During processing, the quantities of each constituent and process conditions will be shifted slightly to take into account varying amounts and types of contaminants.

#### PROCESS SCHEMATIC

A schematic of the proposed process is presented in the attached flow chart. It shows the major pieces of process

equipment starting with the film slurry being fed to the reactor through the storage of product terephthalic acid. This system is a continuous processing version of the pilot plant that recovered silver and terephthalic acid from outdated x-ray film.

The operation of the system is as follows: The film, caustic, from storage (D3, G3) and water is charged into the reactor (C1). Hot heat transfer fluid is introduced into the reactor jacket (E1) to bring the reactor to the operating temperature during startup and hold it at a temperature during processing. An air compressor (K1) and surge bottle (C3) introduce air into the reactor to control odor and burn off the cyanide and contaminants. Process gas leaving the reactor passes through a condenser system (E2) which recovers hot condensate and heats fresh water to recover energy. A back pressure control valve vents the non condensable process gases and establishes the reactor pressure. The reactor agitators maintain a uniform liquor/film slurry and enhances the gas/liquid mass transfer to provide air for the combustion reactions.

The hot liquor is withdrawn from the reactor under pressure, cooled to below the flash point in a heat exchanger (E3), and discharged through dump valves to a holding tank (D1). The reactor discharge liquor preheats the reactor feed saving energy.

The reactor liquor containing some residual solids is pumped from the agitated surge tank through a filter (Y1) before passing into the acid neutralization reactor (D2). The filter removes solids which would be contaminants in the product TPA formed later in the process.

In the neutralizer, sulfuric acid is added from storage (D4, G4) to the basic liquor and sodium terephthalate is formed in the reactor. In the presence of sulfuric acid, the sodium terephthalate reacts to form soluble sodium sulfate and insoluble terephthalic acid. This slurry is pumped to a vacuum filter (Y2).

The vacuum filter separates the liquor from the insoluble terephthalic acid (TPA). In the process, the TPA filter cake is formed on a moving belt. Once the cake is out of contact with the liquor, it passes under a series of wash heads which rinse the cake with fresh water, thus removing residual reactor liquor which contains sodium sulfate, excess sulfuric acid, and other soluble organic and inorganic constituents. This clear liquor is withdrawn from the filter through a vacuum system

(H1, C4, G7) and discharged. The washed cake is then conveyed (T3) into a dryer (Y3).

The water in the TPA filter cake is evaporated in a dryer which uses energy drawn from the heat transfer loop (F1, G6). The design is such that the wet cake is moved through the unit and discharges a dried product of pure TPA which is then conveyed (T2) to storage (T1) for sale.

In support of the principal flow path described, the process includes a number of subsystems. These include:

- o An air compressor with intercoolers, surge tank and controls to supply air to the reactor (K1, C3).
- o A sodium hydroxide system for the transfer and metering of sodium hydroxide from tankage (either railcar or truck) into the reactor (D3, G3).
- o A heat transfer loop consisting of a furnace/heater, expansion tank, and circulating pumps for providing energy for reactor heatup and temperature maintenance and energy required for the evaporation of water in the dryer (F1, G6).
- o A sulfuric acid system for the transfer and metering, under pH control, of acid from tankage into the neutralization reactor (D4, G4).
- o A vacuum system for the removal and discharge of waste process liquor from the TPA filter (H1, C4, G7).

In addition to the above equipment, a quality control laboratory will be provided to monitor the feed and product materials at each step of the process.

TPA RECOVERY PROCESS  
MASS BALANCE SUMMARY  
Basis -- 100 lb feed

MATERIAL	Reactor In	Reactor Out	Filter Cake**	Filter Liquid	Acid Reactor In	Acid Reactor Out	Acid Filter Cake*	Acid Filter Liquor**	Dryer Cake	Dryer Vent*
SCRAP:	(100.00)									
Mylar	90.00									
Inorganic/Dirt	3.00	3.00	3.00							
Combustible	7.00									
Reagents:										
Sodium Hydroxide	666.70	585.99	5.52	587.22	587.22	587.22	179.55	1132.13	0.00	179.55(g)
Sulfuric Acid	52.50				64.31	.60	.01	.59	.01	
Air:	(855.5CF)									
Oxygen	16.00									
Nitrogen	52.70	52.70(g)								
Products:										
Water		6.75				4.46				
Sodium Terephthalate		98.44	.92	97.52	97.52					
Terephthalic Acid						77.09	77.09		77.09	
Sodium Acetate		10.25	.10	10.15	10.15					
Acetic Acid						7.43	.02	7.41		.02(g)
Sodium Bicarbonate		21.00	.20	20.80	20.80					
Carbon Dioxide						10.89(g)				
Sodium Sulfate						92.31	.23	92.08	.23	
ethylene Glycol		29.06	.27	28.79	28.79	28.79	.07	28.72		.07(g)
Other:										
Water (vapor off)		80.71(g)								
Water (TPA filter wash)								(720.00)		
TOTALS	887.90	887.90	10.10	744.48	808.79	808.79	256.97	1260.93	77.33	179.64(g)

\* Product Stream

\*\* Waste Stream



APPENDIX F  
BANK LETTER OF REFERENCE



CitizensBank



William D. McGuire  
Vice President

February 13, 1984

Mr. Daniel L. Eberhardt  
MRC ENTERPRISES, INC.  
1717 Webster Avenue  
Chicago, IL 60614

RE.: Cyanide Contaminated Film Chip Project

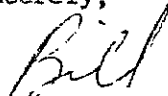
Dear Dan:

We appreciate your advising us as to the exciting prospects concerning the possibility of a contract being entered into with the State of Illinois. There certainly has been a good deal of information discussed about this problem.

Our Bank would certainly be interested in reviewing the financial requirements of this Project in order to, hopefully, assist you with your credit needs.

Due to your excellent relationship with us to date involving a sizeable line of credit as well as equipment accommodations, I feel that a realistic proposal from you would be positively considered. I will look forward to hearing more about the Project to see if we can be of assistance.

Sincerely,



William D. McGuire  
Vice President

WDM/ds